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FINAL REPORT ON ONR CONTRACT N00014-85-K-0177

Title: PREPARATION OF TRANSPARENT FAR INFRARED PHOSPHIDES AND CHALCOGENIDES

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SUMMARY OF WORK DONE DURING CONTRACT PERIOD

During the past five years the ONR program at Brown University dealing with the preparation of transparent far infrared phosphides and chalcogenides has concerned itself with the following materials:

1. ZnSiP2 and ZnGeP2. Single crystals of these compounds were grown and their spectral response, stability in a high temperature flowing oxygen atmosphere, as well as hardness, were determined. The substitution of arsenic for phosphorous in ZnGeP2 was attempted and although some substitution was achieved, there was no improvement in the desired properties.

2. Preparation and characterization of Cu2B(II)C(IV)X4[B(II) = Zn,Cd; C(IV) = Si,Ge; X = S,Se. A number of these quaternary chalcogenides crystallizing with the wurtz-stannite structure have been prepared and characterized. Cu2ZnGeS4 and Cu2ZnSiS4 transmit in the infrared beyond 12 microns. Cu2ZnGeS4 was stable in air up to 620°C and also was the hardest of all the materials studied.

3. Single crystals of members of the system $(ZnSe)_{1-x}GaP_x$ were grown by chemical vapor transport using iodine as the transport agent. The IR spectra of $(ZnSe)_{.905}(GaP)_{.095}$ is not appreciably changed from that of pure ZnSe; however, the hardness and stability towards oxidation are greatly enhanced.

4. The compounds $CuGaS_2$, $CuAl_2$ have been also prepared as single crystals and their properties studied. They all crystallize with the chalcopyrite structure. $CuAlS_2$ has higher thermal stability and hardness than $CuGaS_2$, but its IR transmission range is smaller.

5. In an attempt to prepare infrared materials which have superior properties to those of the II-VI chalcogenides, members of the system $Zn_{1-x}Cd_xGa_2S_4 (1 \geq x \geq 0)$ were prepared and their infrared transmission, hardness and stability were measured. Whereas both $CuGa_2S_4$ and $CdGa_2S_4$ transmitted in the infrared and have reasonable measured values for thermal stability and hardness, there is little improvement achieved by solid solutions.

6. Crystals of zinc sulfide have been doped with small amounts of iron, cobalt and nickel. It was found that these materials had the same long wavelength IR transmission characteristics of pure ZnS. Furthermore, the substitution of small amounts of transition metals for zinc ($\sim$ 1 at %) significantly increased the hardness of ZnS. These materials may be useful for the development of IR windows in the 8-12 micron range.

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Technical Report 6. Preparation and Characterization of SnS_2 March 1988.

Technical Report 7. Growth and Characterization of $CuGaS_2$, $CuAlS_2$ and $CuGa_{0.9}Al_{0.1}S_2$ Single Crystals, March 1988.

Technical Report 8. Growth and Characterization of Zinc and Cadmium Thiogallate, September 1988.

Technical Report 9. Growth and Characterization of Nickel-Doped ZnS Single Crystal, September 1988.

Technical Report 10. Preparation of Compounds with the Tetrahedral Structure which Transmit in the Far Infrared, May 1989.

Technical Report 11. Redetermination of Crystal Structure of Zinc Thiogallate, May 1989.

Technical Report 12. Growth and Characterization of Zinc Sulfide Films by Conversion of Zinc Oxide Films with H_2S, September 1989.

Technical Report 13. The Preparation and Properties of Cobalt-Doped II-VI Chalcogenides, September, 1989.

Technical Report 14. Preparation and Characterization of $Cu_2ZnGeS_{4-y}Se_y$, January 1990.

Technical Report 15. Preparation and Properties of Iron Doped II-VI Chalcogenides, March 1990.